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(54) Title: RADIATION CURABLE SATURATED POLYOLEFIN PRESSURE-SENSITIVE ADHESIVE		
(57) Abstract <p>Pressure-sensitive compositions comprise (1) one or more copolymers of α-olefins of which 85-99 mole percent of one or more straight chain α-olefins having 2 to 10 carbon atoms of which at least 70 % have 6 to 10 carbon atoms and (2) 15 to 1 mole percent of one or more α-olefins having 6 to 20 carbon atoms including at least one methylidene group. The compositions, on radiation, provide adhesive films useful in adhesive applications especially for applications where the bonded articles will be used at elevated temperatures.</p>		

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RADIATION CURABLE SATURATED POLYOLEFIN
PRESSURE-SENSITIVE ADHESIVE

FIELD OF THE INVENTION

5 This invention relates to radiation curable poly(α -olefin) pressure-sensitive adhesive compositions. The invention relates particularly to radiation curable poly(α -olefin) pressure-sensitive adhesive compositions having improved resistance to
10 oxidative degradation and superior cohesive strength particularly at elevated temperatures, without use of tackifiers, and to laminated structures made therefrom.

BACKGROUND OF THE INVENTION

15 A continuing need in the pressure-sensitive adhesive (PSA) art is achievement of better control over various mechanical and process properties so that adhesives can be "tailor-made" for specific, highly demanding end-use applications such as packaging,
20 medical, and masking tapes. These applications require a proper balance of properties, and this balance changes with the particular end-use.

 Among the earliest polymers to provide a reasonable balance of the properties required for
25 satisfactory PSA performance were the natural and synthetic rubbers. However, these PSAs had poor aging properties, and the art quickly recognized the need to eliminate ethylenically-unsaturated groups from the polymer backbone of rubber adhesives in order to
30 improve their oxidative stability.

 With the discovery of ZN catalysts, it became possible to polymerize α -olefin monomers to high molecular weight. The homopolymers of the C₆-C₁₀ α -olefins were naturally tacky and therefore good
35 candidates for PSAs since they also had low toxicity, good aging and favorable environmental stability (i.e., low oxidation). These homopolymers were chemically

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inert, resistant to plasticizer migration, and relatively inexpensive. However, they had poor cohesive strength and therefore lacked characteristics necessary for use at elevated temperatures.

5 Radiation curing has been frequently used to chemically crosslink the polymeric component of adhesives in attempts to increase the cohesive strength of coated adhesive films. The results have been unsatisfactory because competing crosslinking and
10 degradation (chain scission) reactions occur simultaneously. Therefore, in some PSA systems, especially those formulated from polymers containing propylene, radiation curing leads to a loss of cohesive strength and shear adhesion.

15 Adhesives derived primarily from C₆ or larger α -olefins are well known in the art. U.S. Patent No. 3,542,717 describes poly(α -olefin) adhesive compositions comprising mixtures of polyolefin copolymers derived from olefin monomers with different
20 molecular weights (i.e., olefins having 11-20 carbon atoms, and different α -olefins having 4-20 carbon atoms). The resulting adhesive has high shear and peel adhesion at room temperature, but at high temperatures cohesive strength and shear adhesion are unacceptably
25 low for most applications.

U.S. Patent No. 3,635,755 describes PSA polyolefins suitable for use as single component PSAs for surgical tapes that are substantially non-allergenic. Such adhesives can be made from
30 homopolymers of the C₆ to C₁₁ α -olefins or from interpolymers of C₂ to C₁₆ α -olefins having an intrinsic viscosity of 1.5 to 7.0, a Williams' plasticity of 0.8 to 4.0, and an acetone/heptane soluble fraction of less than 25% by weight. Tapes made from these adhesives
35 have low shear adhesions that facilitate non-irritating removal from the skin. However, this low shear

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adhesion is unsuitable, for example, for masking or packaging tape applications.

U.S. Patent Nos. 3,954,697 and 4,178,272 describe hot-melt adhesives useful for sealing polyethylene
5 films derived from copolymers of propylene and C₆-C₁₀ α-olefins. The '697 patent teaches that while C₆ or C₈ α-olefin copolymers are permanently tacky, they have poor cohesive strength and consequently lack shear adhesion. Therefore the higher α-olefins must be copolymerized
10 with propylene in order to meet "the critical property requirements for a pressure-sensitive adhesive material". One such a property, cohesive strength, is discussed in col. 1, lines 34-48. The copolymer must contain more than 40 mole % propylene, especially if
15 static shear is to exceed 1000 minutes. The '272 patent describes compositions comprising a ZN catalyst system and discloses process conditions useful in preparing the "tacky" copolymers required for PSAs. Also disclosed are stereo-regulating three-component ZN
20 catalyst systems that produce high molecular weight, crystalline block copolymers unsuitable for PSA applications (col. 2, lines 39-65), but are stated to be useful in sealing bags, cartons, and on an adhesive for floor tiles.

25 This approach is further advanced in U.S. Patent No. 4,288,358 which describes hot-melt adhesive compositions containing terpolymers of propylene, either 1-butene or 1-pentene, and C₆-C₁₀ α-olefins; tackifying resins; and plasticizing oils, in yet
30 further efforts to simultaneously optimize the adhesive and process properties of these compositions.

While these references teach optimized processing conditions for preparation of hot melt adhesives that are readily coatable or extrudable at the melt
35 temperature, these materials have poor PSA properties. In particular, they have poor adhesion under shear. To be useful, high temperature masking tapes used in the

automotive industry must have good "shear adhesion" at elevated temperatures. Attempts to improve these propylene containing poly(α -olefin) adhesives of the references by radiation crosslinking have led to a
5 degradation of PSA properties, such as shear adhesion.

U.S. Patent Nos. 2,933,480 and 3,933,769 describe a process for copolymerizing mixtures of α -olefins and non-conjugated diolefins to yield sulfur-vulcanizable unsaturated elastomers described as "rubber-like" or
10 "rubbery".

U.S. Patent No. 4,990,585 discloses hexene- $\frac{1}{2}$ -methyl-pentene-1 random copolymer and process for producing the same. The polymer is useful as rubber vibration insulators, modifiers for plastics and
15 rubbers and as adhesives.

U.S. Patent No. 5,112,882 describes adhesive tapes prepared using radiation curable poly(α -olefin) pressure-sensitive adhesive compositions having superior cohesive strength and shear adhesion. The
20 polyene- and optional tackifier-containing compositions can have desirable peel adhesion, shear strength, and stability against oxidative degradation at low and moderate temperatures.

25 SUMMARY OF THE INVENTION

Briefly, the present invention provides a radiation-curable α -olefin copolymer composition that comprises:

- a) at least one copolymer comprising the reaction
30 product of
- 1) 90.1 to 99.9 mole percent of one or more straight chain α -olefins having 2 to 32 carbon atoms of which at least 70% have 6 to 10 carbon atoms, and
 - 35 2) 9.9 to 0.1 mole percent of one or more α -olefins having 6 to 20 carbon atoms including at least one methylidyne group (a one carbon-

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containing group having a hydrogen atom on a tertiary carbon atom) present in a branched or cyclic group of carbon atoms; and

- b) optionally, sufficient photoactive crosslinking agent to crosslink the composition upon exposure to actinic radiation.

After curing, the composition provides a pressure-sensitive adhesive preferably having peel adhesion of 35 N/dm or more and cohesive stability at temperatures above 120°C. The adhesive can be of particular use in tapes required for high temperature masking and hot melt adhesive applications.

Preferably, the polymer of the present invention has a glass transition temperature (T_g) in the range of -70°C to 0°C, more preferably in the range of -60 to -20°C, and an inherent viscosity in the range of 0.4 to 9.0 dl/g, more preferably 0.5 to 6.0 dl/g, and most preferably 1.5 to 4.0 dl/g. Number average molecular weights of the polymers are in the range of 5,000 to 50,000,000, preferably 50,000 to 5,000,000.

The copolymers of the present invention do not contain residual ethylenic-unsaturation but do contain pendant side groups having readily reactive hydrogen atoms on tertiary carbon atoms that, on radiation, preferably in the presence of a photoactive crosslinking agent, leads to crosslinking of the copolymer and thereby improved cohesive strength of the adhesive. Because ethylenic-unsaturation is not present in the copolymers, cured adhesives prepared from them have improved elevated temperature oxidative stability as well as excellent adhesion and chemical/electrical resistance, and they are physiologically inert. These properties make them excellent pressure-sensitive adhesives for a wide range of applications where it is desirable to have independent control of peel and shear adhesion.

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It is believed that the background art does not teach PSA compositions comprising one or more poly(α -olefin)s which can be copolymers, including terpolymers, or tetrapolymers, derived from α -olefin monomers containing 6 to 10 carbon atoms and no polyenes and optionally further comprising one or more photoactive crosslinking agents, the compositions having been radiation-cured to yield adhesive films having improved resistance to oxidative degradation as well as possessing substantial high temperature shear strength.

The present invention provides an α -olefin copolymer-containing pressure sensitive adhesive composition that is radiation curable. The α -olefin copolymer-containing adhesive composition can be cured to yield a PSA adhesive film with an improved balance of peel and shear adhesion. The peel and shear adhesion values are capable of being varied independently to achieve desired values. Adhesive layers of the invention preferably have peel values greater than 35 N/dm and resistance to oxidative degradation at temperatures up to at least 200°C. Radiation curing can be achieved by ultraviolet or electron beam radiation. Where electron beam radiation is used for curing, no photoactive crosslinking agent is needed.

The adhesive of the invention can be applied to appropriate substrate surfaces by a wide range of processes, i.e., solution coating, solution spraying, hot-melt extrusion, emulsion coating, etc., to make adhesive tapes, adhesive transfer films, and the like. Since the polyolefin composition of the invention is free of unsaturation either in the backbone or in pendant groups of the copolymer, the thermal stability of the compositions is superior to compositions containing polyolefins having unsaturation. Further, gelation during hot melt extrusion of the copolymer

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composition of the invention is minimal or does not occur.

As used in this invention:

" α -olefin copolymer" means a random polymer
5 derived from two or more terminal monoethylenically-unsaturated monomers;

"straight-chain α -olefin" means a linear hydrocarbon having no branching and only one terminal ethylenic-unsaturation group and no other functional
10 groups;

" α -olefin having at least one methylidyne group" means a hydrocarbon having only one terminal ethylenically-unsaturated group and no other functional groups and having pendant to the ethylenically-
15 unsaturated group, a group having a carbon atom that is attached to three other carbon atoms and to a hydrogen atom;

"film" means a layer or a support and a self-supporting layer;

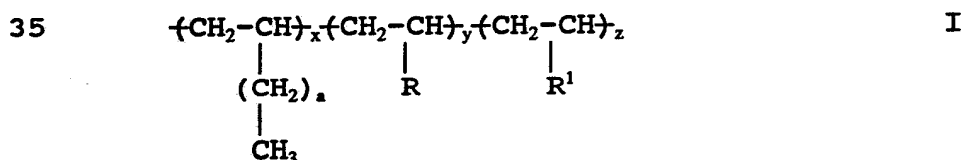
20 "photoactive crosslinking agent" means a compound which, under the influence of radiation, connects polymer chains and becomes incorporated therein; this increases the molecular weight of the adhesive and thus its cohesive strength without unduly affecting its
25 compliance or other PSA properties;

"actinic radiation" means electromagnetic radiation, preferably in the ultraviolet range; and

"lower alkyl" means C₁ to C₅ alkyl group.

30 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The radiation-curable α -olefin copolymers of the invention preferably have general formula I:

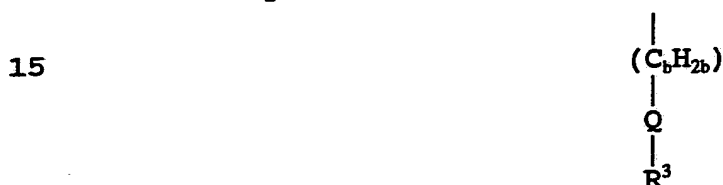


wherein

R is hydrogen or a lower alkyl group;

R¹ is a monovalent organic group that is free of
 5 ethylenic-unsaturation and contains at least
 one

methyldiyne group, $\begin{array}{c} | \\ -\text{CH} \\ | \end{array}$, having 4 to 30, and
 10 preferably 4 to 18 carbon atoms, optionally
 containing an oxygen or silicon atom that is
 catenated between carbon atoms, and
 preferably having the structural formulae:



20 in which b is an integer having a value of 1
 to 5; Q is a connecting linkage selected from
 a single bond, -O- and divalent groups
 selected from the group consisting of an
 25 arylene group having 6 to

15 carbon atoms and $\begin{array}{c} \text{R}^4 \\ | \\ -\text{Si}- \\ | \\ \text{R}^4 \end{array}$, in which each R⁴ is

30 independently a lower alkyl group of 1 to 4
 carbon atoms or R³; and R³ is a methyldiyne
 group-containing group having the structural
 formula:



40 in which each R⁵ is independently an alkyl
 group having 1 to 4 carbon atoms or both R⁵s
 together provide an alkylene group forming
 with the methyldiyne group to which it is
 attached a 5- or 6-membered ring of carbon

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atoms, with the provision that when Q is arylene, R³ can also be methyl or ethyl, and b can also be zero;

5 a is an integer having a value of 3 to 7, inclusive;

x, y, and z are numbers designating the relative molar amounts of monomer units comprising the backbone chain of the copolymer, the sum of (x + y + z) being about 35 to 400,000; z being 1 to 15%, preferably 2 to 10%, and most preferably 2 to 6% of the sum (x + y + z); y being 0 to 30% of the sum (x + y + z), and x being 64 to 99%, preferably 90 to 98%, and most preferably 94 to 98% of the sum (x + y + z).

15 The copolymers of the invention are prepared by copolymerizing one or more straight chain α -olefins and one or more methylidyne group-containing α -olefins.

Straight chain α -olefins that can be used have six to ten carbon atoms, namely, 1-hexene, 1-heptene, 1-
20 octene, 1-nonene, and 1-decene.

Optionally, up to 30 mole percent, preferably 1 to 10 mole percent, of total α -olefins of straight chain α -olefins having two to five carbon atoms can be used, namely, ethene, 1-propene, 1-butene, and 1-pentene.

25 Suitable methylidyne group-containing α -olefins that can be used have 6 to 20 or more carbon atoms including, 4-methyl-1-pentene, 5-, and 4-methyl-1-hexene, ethenylcyclopentane, 6-, 5-, and 4-methyl-1-heptene, 4,5-dimethyl-1-hexene, 4-ethyl-1-hexene, 30 ethenylcyclohexane, 7-methyl-1-octene, 8-methyl-1-nonene, 4,6-dimethyl-1-heptene, allylcyclohexane, 2-ethenylbicyclo[2.2.1]heptane (2-ethenylnorborane, this α -olefin has 2-methylidyne groups), 2-ethenyl-6-methylbicyclo[2.2.1]heptane (this α -olefin has 2
35 methylidyne groups), 2-ethenyl- (6-methylbicyclo[2.2.1]heptane this α -olefin has 3 methylidyne groups), 2-(3-

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- propenyl)bicyclo[2.2.1]heptane (propenylnorborane, this α -olefin has 2 methylidyne groups), 3-(3-propenyl)-
2,6,6-trimethylbicyclo[3.1.1]heptane (3-propenylpinane, this α -olefin has 3 methylidyne groups), 1-
5 ethenylpentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (ethenylcubane, this α -olefin has 7 methylidyne groups), 1-ethenyltricyclo[3.3.1.1^{3,7}]decane (ethenyladamantane, this α -olefin has 3 methylidyne groups), and 1,2-dimethyl-5-
10 ethenyltricyclo[3.3.1.1^{3,7}]decane (1,2-dimethyl-5-ethenyladamantane, this α -olefin has 2 methylidyne groups).

Other methylidyne group-containing α -olefins that are suitable for use in the copolymers of the invention
15 are the arylene, the catenary oxygen, and the catenary silicon group-containing α -olefins, such as, for example: 4-(1-methylethyl)-1-(3-propenyl)benzene, 4-(2-methylpropyl)-1-(3-propenyl)benzene, 2-(1-methylethyl)-4-pentyl-3-propenyl-naphthalene, 4-methyl-3-
20 propenylbenzene, 3-(2-methylpropoxy)-1-propene, 4-(2-methylpropoxy)-1-butene, 3-cyclohexoxy-1-propene, dimethyl(1-methylethyl)-3-propenylsilane, bis(1-methylethyl)methyl-3-propenylsilane, and bis(1-methylethyl)methyl-4-butenylsilane.

25 The α -olefins can be copolymerized in the presence of Ziegler-Natta (ZN) catalysts over a wide range of temperatures, e.g., 0 to 140°C, preferably 30 to 90°C. The polymerization can be done in bulk or in inert solvents. Suitable examples of inert solvents include,
30 but are not limited to, aliphatic, aromatic, and cycloaliphatic hydrocarbon solvents, i.e., hexane, heptane, benzene, toluene, cyclopentane, and cyclohexane. The amount of catalyst used is preferably in the range of 0.1 to 5 grams per kilogram of monomer, more preferably 0.2 to 2 grams per kilogram of monomer.
35 The copolymerization of α -olefins and polyene monomers is often slow and results in poor yields of polymer

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whereas the copolymerization of α -olefins and methlidene-containing olefins goes rapidly and in excellent yield.

Use of ZN catalysts to make homopolymers from α -
5 olefin monomers, and copolymers from mixtures of α -olefin and non-conjugated polyene monomers is old in the art and is not the subject of this invention. ZN polymerizations are summarized in Odian, G., "Principles of Polymerization", Ch. 8.4 (Second
10 Edition, J. Wiley & Sons, New York, 1981). For a more detailed discussion of the polymerization of α -olefins, see Boor, J., "Ziegler-Natta Catalysts and Polymerizations", Ch. 19 (Academic Press, NY, 1979).

NMR analysis of the copolymers shows the absence
15 of ethylenic-unsaturation. Useful copolymers can also be made by hydrogenation, by processes known in the art, of unsaturated poly(α -olefins).

Copolymers can be made from one or more straight
chain α -olefins and from 0.1 to 9.9 mole percent of one
20 or more methylidyne group-containing α -olefins. By varying the composition and ratios of these monomers, copolymers can be prepared that yield PSA films with peel, gel content, and shear adhesive properties required for various specialized end-use applications.

25 Pressure-sensitive adhesive films can also be prepared by adding a photocrosslinking agent to the copolymer to form an adhesive composition, and coating the composition onto a substrate. Suitable photocrosslinking agents include, but are not limited
30 to: aldehydes, such as benzaldehyde, acetaldehyde, and their substituted derivatives; ketones such as acetophenone, benzophenone and their substituted derivatives, particularly the 4-alkylbenzophenones wherein the alkyl group has 1 to 18 carbon atoms such
35 as methyl, ethyl, butyl, octyl, dodecyl and octadecyl, and commercially available derivatives such as Sandoray 1000™ (Sandoz Chemicals, Inc., Charlotte, NC); quinones

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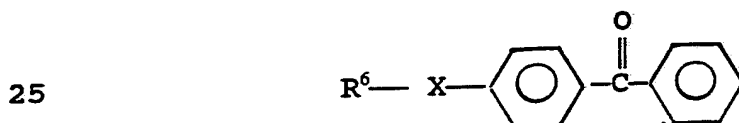
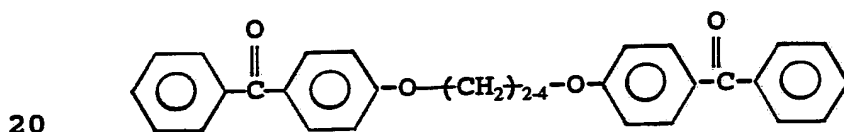
such as the benzoquinones, anthraquinone and their substituted derivatives; thioxanthenes such as 2-isopropylthioxanthone and 2-dodecylthioxanthone; and certain chromophore-substituted halomethyl-sym-

5 triazines such as 2,4-bis-(trichloromethyl)-6-(3',4'-dimethoxyphenyl)-sym-triazine. Photoactive crosslinking agents that are preferred because (1) they are particularly effective in bringing about rapid

10 gelation of the adhesive composition on application of radiation, (2) of their low vapor pressure, and (3) of their thermal stability, are polyfunctional benzophenones (that is, compounds having an aliphatic,

aromatic, nitrogenous, silicic, and hetero atomic nuclei to which two to four benzoylphenoxy groups are

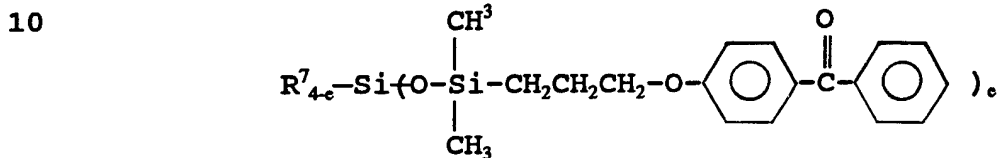
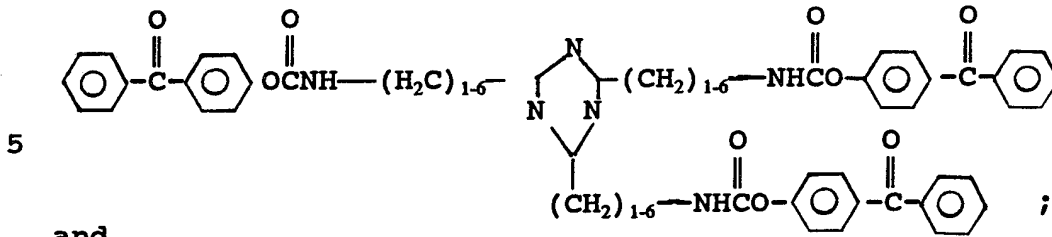
15 attached). Examples of such compounds include:



in which R^6 is hydrogen or an alkyl group having 1 to

30 18 carbon atoms; and X is $-O-$, $-\overset{\text{O}}{\parallel}{\text{C}}-$, $-\overset{\text{O}}{\parallel}{\text{N}}\text{C}O-$, or $-\text{CH}_2-$;

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in which R^7 is an alkyl group having 1 to 18 carbon atoms and e is the integer 2, 3, or 4.

The concentration of photoactive crosslinking agent that can be present is in the range of 0.05 to 6.0, preferably 0.1 to 2 percent by weight of the curable copolymer, and more preferably 0.5 to 1.5 percent by weight.

The adhesive composition of the present invention can be coated from solution by any of the various coating processes well known in the art, such as knife coating, roll coating, gravure coating, curtain coating, etc. Useful coating thicknesses for the present invention are in the range of 0.5 to 15 mg/cm², preferably in the range of 2.0 to 7.0 mg/cm². Furthermore, some of the compositions of the invention can be applied by various extrusion coating processes with no solvent present, thereby eliminating environmental and toxicity problems associated with solution coating processes.

The adhesive composition can be cured using a source of actinic radiation of sufficient energy (i.e., wavelength range) to generate free radicals when incident upon the particular photoactive crosslinking agent selected for use in the composition. The preferable wavelength range for the photoactive crosslinking agents disclosed above is 400 to 250 nm. The radiant energy in this preferred range of

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wavelengths required to crosslink the adhesive film of the invention is 100 to 1500 millijoules/cm² and more preferably 200 to 800 millijoules/cm². Details of the photocure process are disclosed in U.S. Patent Nos. 5 4,181,752 and 4,329,384. Because the adhesive composition of the present invention contains a polymer, the pre-polymerization (i.e., the making of a syrup) step disclosed in the '752 and '384 patents is not required and is omitted in photocuring the 10 compositions of the present invention.

The adhesive composition, without any crosslinking agent present, can also be cured using electron beam (E-beam) radiation. The preferred dosage required to crosslink the adhesive film of the invention is from 1 15 to 20 megrads (Mrads), preferably from 2 to 10 Mrads. Details of suitable process for E-beam curing substrates that have been coated with adhesive composition of the invention can be found in U.S. Patent No. 4,533,566, which is hereby incorporated 20 herein by reference.

The crosslinked adhesive films preferably have a gel content in the range of from 2 to 95 weight percent, more preferably from 30 to 80 weight percent, and most preferably from 50 to 70 weight percent when 25 the gel content has been corrected for soluble tackifying resins and other additives as hereinafter described.

The crosslinking agent, when present, can extract tertiary hydrogen and allows open-bonded segments to 30 join and form a crosslinked polymer. Where the crosslinking agent is polyfunctional, it can extract tertiary hydrogen at more than one site and can become incorporated into the polymer by forming a linking group in the polymer.

35 Addition of one or more tackifying resins to the inventive composition can provide a PSA having improved tack, lower melt viscosity, improved coatability, good

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heat stability, and improved peel adhesion. Shear adhesion of the tackified compositions can be enhanced by radiation cure with no loss of peel adhesion. High internal strength of the adhesive is necessary in box
5 sealing tapes and masking applications in the automotive industry.

Compatible tackifying resins useful in the radiation curable adhesive compositions of the invention include resins derived by polymerization of
10 unsaturated hydrocarbon monomers, having five to nine carbon atoms, polyterpenes, synthetic polyterpenes, and the like. Hydrocarbon tackifying resins can be prepared by polymerization of monomers consisting primarily of olefins and diolefins and include, for
15 example, residual by-product monomers of the isoprene manufacturing process. These hydrocarbon tackifying resins typically exhibit Ball and Ring Softening Points of from about 80°C to about 145°C; Acid Numbers of from about 0 to 2, and Saponification values of less than
20 one. Examples of such commercially available resins based on a C₃ olefin fraction of this type are Wingtack™ 95 and Wingtack™ 115 (Wingtack Plus) tackifying resins available from Goodyear Tire and Rubber Co. Other hydrocarbon resins include Regalrez™ 1078 and Regalrez™
25 1126 tackifying resins available from Hercules Chemical Co. Inc., Wilmington, DE; Arkon resins, such as Arkon™ P115 tackifying resin, available from Arakawa Forest Chemical Industries, Chicago, IL; and Escorez™ resins available from Exxon Chemical Company.

30 Other suitable tackifying resins include the terpene polymers, such as polymeric resinous materials obtained by polymerization and/or copolymerization of terpene hydrocarbons such as the alicyclic, mono, and bicyclic monoterpenes and their mixtures, including
35 carene, isomerized pinene, terpinene, terpentene, and various other terpenes. Commercially available resins of the terpene type include the Zonarez™ terpene B-

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series and 7000 series tackifying resins available from the Arizona Chemical Corp., Wayne, NJ. Typical properties reported for the Zonarez™ terpene resins include Ball and Ring Softening Points of about 55°C to 125°C (ASTM E28-67), Acid Numbers of less than one (ASTM D465-59) and Saponification Numbers of less than one (ASTM D464-59). The terpene resin used in examples below is a poly(beta-pinene) resin, Piccolyte™ A115 resin available from Hercules Chemical Co. Inc., which has a Ball and Ring Softening Point of 115°C, and Acid Number of one, and Iodine Number of 190.

Where stability at elevated temperatures is needed, saturated tackifying resins are used.

The total amount of optionally present tackifying resins in the composition is more than 0 to 150 parts by weight, more preferably 5 to 50 parts, and most preferably 25 to 35 parts by weight per 100 parts of polymer by weight. Saturated tackifying resins such as Regalrez™ 1078 resin and Arkon™ P115 resin are preferred because they yield a higher gel content than upon equivalent treatment by an activated crosslinking agent.

The radiation-cured saturated polyolefin pressure-sensitive adhesive of the invention is prepared by a method comprising the steps of:

- a) providing a composition comprising
 - 1) a copolymer having general formula I,
 - 2) optionally and preferably an effective amount of a photoactive crosslinking agent,
 - 3) optionally a tackifying agent, which preferably is a saturated tackifying agent;
- b) coating the composition onto a substrate;
- c) exposing the coated composition to actinic or E-beam radiation to effect crosslinking of

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the composition and provide said radiation-cured pressure-sensitive adhesive, with the proviso that when the crosslinking is effected by actinic radiation there is present an effective
5 amount of photoactive crosslinking agent.

Minor amounts of additives can also be included in the composition to provide adhesives for special end uses. Such additives may include pigments, dyes, plasticizers, fillers, stabilizers, ultraviolet
10 absorbers, anti-oxidants, processing oils, and the like. Amount of additives used can vary from 0.1 to 50 weight percent depending on the end use desired.

The adhesive composition of the present invention can be coated onto a wide range of substrate materials,
15 examples being polymeric supports such as polyethylene terephthalate (PET) (Dupont Chemical Co., Wilmington, DE), and biaxially oriented polypropylene (BOPP) (Toray Chemical Co., Ltd., Tokyo, Japan, or Mobil Oil Co.; woven and non-woven fabrics, metals and metal foils
20 such as aluminum, copper, lead, gold, and the like; paper; glass; ceramics; and composite materials comprised of laminates of one or more of these materials. Pressure sensitive adhesive tapes and transfer films are preferred articles of the invention.

25 Another embodiment of the invention comprises a laminated structure of at least a first and a second substrate such as polyethylene and polypropylene, the substrates being joined by a layer of the adhesive composition of the invention. At least one of the
30 substrates is capable of transmitting actinic or electron beam radiation so that the adhesive layer may be cured.

In some applications primers may be useful for improving the adhesion of the adhesive to some
35 substrates. Useful primers for the practice of the present invention include a triblock copolymer of styrene-ethylene/butylene-styrene grafted with maleic

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anhydride (Kraton™ G-1901X copolymer, Shell Chemical Co.) and a combination of amorphous polypropylene and Kraton™ G1901X copolymer. Release liners (such as described in U.S. Patent Nos. 4,386,135, 3,957,724, and 2,532,011) form a special class of substrates on which the composition of the invention can be coated and subsequently radiation cured to form adhesive transfer films.

10 Test Methods:

The test procedures used in the examples to evaluate and compare the properties of the PSA compositions and tapes made from them are industry standard tests. These tests are described in detail in various publications of the American Society for Testing Materials (ASTM), Philadelphia, PA and the Pressure Sensitive Tape Council (PSTC), Glenview, IL. References to these standards are also given.

20 Shear Strength (ASTM D-2654-78; PSTC - 7)

The shear strength is a measure of the cohesiveness or internal strength of an adhesive. It is based upon the amount of force required to pull an adhesive strip from a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pressure. It is measured in units of time (minutes) required to pull a standard area of PSA coated sheet material from a stainless steel test panel under stress of a constant, standard load.

The tests were conducted on adhesive coated strips applied to a stainless steel panel such that a 12.7 mm by 12.7 mm portion of each strip was in firm contact with the panel with one end portion of the tape being free. The panel with coated strip attached was held in a rack such that the coated surface of the panel forms an angle of 182° with the vertical tape free end which

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is then tensioned by application of a force of one kilogram applied as a hanging weight from the free end of the coated strip. The 2° greater than 180° is used to negate peel forces, thus ensuring that only the shear forces are measured in order to more accurately determine the holding power of the tape being tested. Time elapsed for each test specimen to separate from the steel panel is recorded as the shear strength.

10 Mode of Failure (MOF)

The time at which the mass falls is called "Shear Test" and is reported as "1000+" if the tape has not failed after 5000 minutes. With each Shear is indicated the mode of failure as follows:

15 PP = pop-off, i.e., 75-100% adhesive failure from steel plate;

Sp = adhesive split: both surfaces completely covered by adhesive.

The pop-off failure mode is preferred because it is indicative of adhesive failure of the adhesive/steel interfacial bond as opposed to cohesive failure of the adhesive. Adhesives of various shear adhesions, all within the range of the present invention (1-1,000 minutes), are preferred depending on end-use applications.

Two specimens of each tape were tested and the shear tests were averaged to obtain the shear value.

Peel Adhesion (ASTM D 3330-78; PSTC - 1 (11/75))

30 The peel adhesion is the force required to remove a PSA coated test specimen from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in Newtons per decimeter (N/dm) width of coated sheet. The procedure followed is:

- 1) A test specimen 25.4 mm wide is applied to a horizontally positioned clean glass test

- 20 -

plate. A 2.2 kg rubber roller is used to press a 12.7 cm length of specimen into firm contact with the glass surface.

- 5 2) The free end of the specimen is doubled back nearly touching itself so the angle of removal is 180°. The free end is attached to the adhesion tester scale.
- 10 3) The glass test plate is clamped in the jaws of tensile testing machine which is capable of moving the plate away from the scale at a constant rate of 2.3 meters per minute.
- 4) The scale reading in Newtons is recorded as the tape is peeled from the glass surface.

15 Inherent Viscosity (ASTM D 2857-70 (Reapproved 1977))

 In order to understand the benefits derived from the teaching of this invention, it is necessary to relate the improvements in shear strength and processability to the molecular weight of the polymeric
20 component of the PSA. The inherent viscosity of 10 ml of 0.5 g/dl polymer solution is measured using a Cannon-Fenske #50 viscometer (available from Cannon Instruments Co., State College, PA) in a water bath controlled at 25°C. The solvent used is specified in
25 the examples.

Percent Gel Test (ASTM D 2616-81)

 The percent gel is used as an indication of cure level. The tapes containing tackifying resins are
30 corrected to the actual percent gel. The corrected percent gel is 100 times the gelled mass divided by the total mass of material that is capable of forming a gelled network. Soluble materials such as tackifiers and uncrosslinked polymers are extracted before
35 determining the gel fraction.

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Crosslinking by actinic radiation or E-beam improves the creep and shear resistance of pressure-sensitive adhesives.

Many important properties of crosslinked pressure-sensitive adhesives vary with the gel content. Hence, determination of the gel content provides a means for controlling the process and thereby raising the quality of the tape.

Extraction tests permit verification of the proper gel content of polyolefin PSAs and they also permit comparison between different crosslinked adhesives and their specific end uses.

Gel Content Determination:

A square test specimen (3.81 cm x 3.81 cm) containing approximately 0.06 g of PSA is cut from a tape and placed in a 120-mesh stainless steel basket measuring approximately 4 x 8 cm. The contents are weighted to the nearest 0.1 mg and then immersed in a capped beaker containing sufficient toluene to cover the specimen. After extraction for 24 to 48 hours, the basket (containing the specimen) is removed, drained, and placed in an oven at 69°C. The basket and specimens are dried to a constant weight and the gel content is determined as follows:

$$\text{Extract \%} = \frac{\text{Weight lost during extraction}}{\text{Weight of original specimen}} \times 100$$

$$\text{Gel content} = 100 - \text{Extract \%}$$

For the tackified pressure-sensitive adhesive tapes, the weight of the tackifier resin was subtracted before calculating the corrected gel content as follows:

$$\text{Percent extract(\%)} = \frac{\text{Weight lost during extraction} \times 100}{\text{Weight of final specimen} - \text{weight of resin}}$$

$$\text{Corrected gel content} = 100 - \text{percent extract}$$

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Two specimens of each tape were tested and the results were averaged to obtain the gel content value.

Panel Test

5 This test is used to evaluate the effectiveness of the adhesive for use as a masking tape at elevated temperatures. Used in this test is an aluminum panel, the test surface of which has a paint to which masking tapes have been adhered, e.g., an automotive
10 basecoat/clearcoat (BC/cc) acrylic enamel paint system or the automotive 50J™ acrylic enamel paint of Ford Motor Co.

Tapes were adhered at room temperature to the test surface, followed by two passes of a 4.5-pound (2-kg)
15 rubber-coated metal roller. After one hour in an air-circulating oven at either 121°C or 150°C, the tape was peeled back while hot at an angle of 45° at an approximate rate of 1.9 m/min across half of the panel. After cooling to room temperature, the tape was peeled
20 from the other half of the panel. The panel was examined visually for any adhesive residue.

Examples

25 Preparation of Copolymer 1

The following reactants were charged in the order mentioned to a dry, argon filled, circulating water jacketed glass reactor equipped with stirrer and condenser: 474 grams 1-hexene, 1971 grams of toluene,
30 18.75 grams 4-methyl-1-pentene (which had been passed through alumina/silica to remove impurities and then dried over molecular sieves), and 2.7 ml of diethylaluminum chloride (1.8 M in toluene). The copolymerization was initiated by the addition of 0.5 g
35 AATiCl₃ (aluminum activated reduced titanium chloride, Stauffer Catalyst). The molecular weight of copolymer was controlled by passing hydrogen at 60 cc/min

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throughout the reaction period. The reaction was maintained at 25°C during the course of the reaction. After 3 hours of the reaction, the copolymerization was quenched and the polymer precipitated in a large excess of methanol to extract the catalyst residues. The methanol solution was then decanted off of the polymer precipitate. The copolymer was stabilized with 0.25 weight % Irganox 1010 antioxidant (available from Ciba Geigy) and dried in a vacuum oven at 70-80°C.

10 There was obtained 320 g (65% conversion) of copolymer having by NMR analysis 1.5 mol percent of 4-methylpentene units and 98.5 mol percent of 1-hexene units. It had an inherent viscosity (IV) of 2.0 dl/g at 0.5 g/dl concentration in hexane at 25°C and a glass transition temperature (T_g) of -44°C. No crystallinity was detected by differential scanning calorimetry (DSC) analysis.

Preparation of Copolymer 2

20 The procedure for the preparation of copolymer 1 was repeated with the exception that a different monomer ratio was used (419 grams of 1-hexene and 74 grams of 4-methylpentene). The copolymerization was run at 50°C for one hour. A tacky amorphous copolymer was obtained in 50% conversion having an IV of 1.5 dl/g and a T_g of -38°C. The copolymer contained 6.2 mole percent of 4-methylpentene.

Preparation of Copolymer 3

30 The procedure for the preparation of copolymer 1 was repeated with the exception that 150 g 1-octene and 12.5 g of 4-methylpentene were used. A tacky amorphous copolymer was obtained in 60% conversion having an IV of 2.3 dl/g, a T_g of -59°C, and 1.7 mole percent of 4-methylpentene.

35 methylpentene.

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Preparation of Copolymer 4

The procedure for the preparation of copolymer 1 was repeated with the exception that 1-decene and 4-methyl-1-pentene were used (150 g of 1-decene and 10 g of 4-methylpentene). A tacky amorphous copolymer was obtained in 65% conversion having an IV of 1.9 dl/g. The copolymer contained 3.0 mole percent of 4-methylpentene.

10 Examples 1-18

Solutions in toluene of each of Copolymers 1, 2, 3, and 4 (radiated and unirradiated), 0.15 or 1.0 weight percent of photocrosslinking agent benzophenone (B), Sandoray 1000™ crosslinker (a substituted benzophenone) (S), 2,4-bis(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine (T), or 2-isopropylthioxanthane (I) were prepared as shown in TABLE I and coated, using a hand-spread coater, onto 25 micrometer (μm) polyethylene terephthalate film (PET) and dried at 80°C to remove toluene to provide an adhesive coating having a dry thickness of about 37.5 μm . The coatings containing the photocrosslinking agent were then exposed to UV radiation under nitrogen for the dose shown and the characteristics of each of the adhesive coatings was determined and is presented in TABLE I, below.

TABLE I shows that unirradiated compositions of the invention were not gelled and the adhesive in tapes prepared using them failed by splitting. Compositions that were irradiated, however, were gelled from about 36 to 80% depending on the particular copolymer, the crosslinking agent and the amount of irradiation. The irradiated tapes prepared from them popped off and did not split.

TABLE I

Ex. No.	Copolymer (Wt%)	PI (Wt%)	Dose mJ/cm ²	Peel Adhesion N/cm	Shear min.	MOF	GEL (%)
5	1	--	--	56	12	sp	0
	1	B(1)	200	39	4	po	55
	1	S(1)	200	43	5	po	61
	1	T(0.15)	200	45	8	po	38
	1	D(1)	200	48	15	po	65
10	2	--	--	57	4	sp	0
	2	B(1)	450	38	4	po	47
	2	S(1)	450	48	6	po	51
	2	I(1)	450	51	10	po	36
	2	T(0.15)	200	51	23	po	55
15	3	--	--	60	1	sp	0
	3	B(1)	450	46	5	po	80
	3	S(1)	450	45	5	po	77
	3	T(0.15)	450	38	6	po	63
20	4	--	--	57	1	sp	0
	4	B(1)	450	46	5	po	78
	4	S(1)	450	52	5	po	76
	4	T(0.15)	450	56	22	po	60

PI is photocrosslinker in which B is benzophenone;
S is Sandoray 1000^m, I is 2-isopropylthioxanthone,
T is 2,4-bis-(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine,
D is 1,10-bis-(4-benzoylphenoxy)decane
MOF is mode of failure in which sp is split and po is pop-off

TABLE II

Ex. No.	Copolymer (Wt%)	PI (Wt%)	Dose mJ/cm ²	Peel Adhesion N/dm	Shear min.	MOF	GEL. (%)
19	1	--	--	71	27	sp	0
20	1	B(1)	450	63	1122	sp	25
21	1	S(1)	900	62	597	po	34
22	1	I(1)	900	62	295	po	19
23	1	T(0.15)	200	64	198	po	31
24	1	D(1)	200	67	550	po	45
25	2	--	--	72(r)	89	sp	0
26	2	B(1)	450	65	254	po	51
27	2	S(1)	900	70	237	po	60
28	2	I(1)	900	63(r)	537	po	50
29	2	T(0.15)	450	59(r)	950	po	60
30	4	--	--	85	65	sp	0
31	4	B(1)	450	73	72	po	65
32	4	S(1)	450	70	165	po	52

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(I) The tackifier used is Regalrez[™] 1078 (hydrocarbon tackifier available from Hercules Chemical Co. PI is photocrosslinker in which B is benzophenone; S is Sandoray 1000[™], I is 2-isopropylthioxanthone, T is 2,4-bis-(trichloromethyl)-6-(3,4-dimethoxyphenyl)-s-triazine, D is 1,10-bis-(4-benzoylphenoxy)decane MOF is mode of failure in which sp is split and po is pop-off

Examples 19-32

Solutions of each Copolymer 1, 2, 3, and 4 with 0.15 or 1.0 weight percent of the photocrosslinking agents B, S, I, and T and 25 weight percent of Regalrez® 1126 tackifier were prepared in toluene, coated, dried, and exposed to UV, under nitrogen for the dose shown as described for copolymers 1-4. The characteristics of each adhesive obtained is given in TABLE II.

TABLE II shows that irradiated adhesive compositions of the invention containing Regalrez™ 1078 tackifier had increased shear and peel adhesion.

Examples 33-45

Coatings prepared in previous examples were examined according to the Panel Test described previously and the results are detailed in TABLE III.

TABLE III shows that masking tapes prepared using the non-tackified adhesive compositions (Exs. 33-42) and the tackified adhesive compositions (Exs. 43-45) left little, if any, residue in panel tests when irradiated with greater than 450 mJ/cm² of UV radiation.

Ex. No.	Adhesive Sample No.	% Residue left on BC/CC panel after 60 min. at		% Residue left on 50J panel after 60 min. at	
		121°C	150°C	121°C	150°C
33	1	100	100	100	100
34	2	5	10	10	10
35	2a	0	2	0	0
36	6	100	100	100	100
37	7a	0	3	0	1
38	11	95	100	100	100
39	12	5	5	7	10
40	12a	0	0	0	0
41	15	75	100	90	100
42	16	5	10	0	10
43	19	100	95	100	100
44	20	10	50	10	25
45	20a	2	0	0	5

2a is same as 2 except that it was exposed to 450
25 mJ/cm²

7a is same as 7 except that it was exposed to 1200
mJ/cm²

12a is same as 12 except that it was exposed to
1200 mJ/cm²

20a is same as 20 except that it was exposed to
1200 mJ/cm²

Example 46

A one-liter reaction vessel equipped with
35 mechanical stirrer was dried overnight at 110°C and
charged with: 450 ml distilled toluene; 200 ml 1-
hexene; 25 g 4-methylpentene-1; and 1 ml of 1.8 molar
(C₂H₅)₂AlCl in toluene. After bubbling H₂ through the

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stirred solution for one hour, 0.15 g of $TiCl_3$ was added. The reaction mixture was allowed to react under these conditions until a slight but significant increase in viscosity was visually observed (about 45 5 minutes).

Then ethylene gas was introduced to the reaction vessel atmosphere. After 2 hours ethylene was bubbled through the reaction mixture for 3 additional hours before quenching with methanol. The product was a 10 pressure-sensitive adhesive containing 5 mole % of ethylene.

The copolymer solution was blended with 15 weight percent Arkon P115 and 1% by weight benzophenone photoinitiator and coated on 0.04 mm thick (1.5 mil) 15 poly(ethylene terephthalate) followed by UV curing. The cured adhesive had a peel strength of 30 N/dm and shear strength of 1320 min as compared to uncured adhesive of the same composition having a peel strength of 30 N/dm and shear strength of 32 minutes.

20

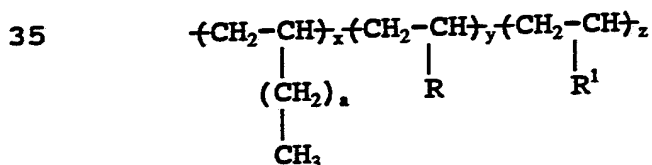
Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this 25 invention is not to be unduly limited to the illustrative embodiments set forth herein.

We claim:

1. A curable composition for providing a hot melt adhesive, or a pressure-sensitive adhesive having 5 peel adhesion of 35 N/dm or more and cohesive stability at elevated temperatures comprising:

- a) at least one copolymer of
- 1) 90.1 to 99.9 mole percent of one or more straight chain α -olefins having 2 to 32 carbon atoms of which at least 70% have 6 to 10 carbon atoms, and
 - 2) 9.9 to 0.1 mole percent of one or more α -olefins having 6 to 20 or more carbon atoms including at least one methylidyne group (a one carbon-containing group having a hydrogen atom on a tertiary carbon atom) present in a branched or cyclic group of carbon atoms; and
- b) optionally, sufficient photoactive crosslinking agent to crosslink the composition upon exposure to actinic radiation;
- c) optionally, more than zero and up to 150 parts by weight of tackifying resin per 100 parts of polymer; and
- d) optionally, an effective amount of at least one additive selected from the group consisting of at least one pigment, dye, plasticizer, filler, stabilizer, ultraviolet absorber, anti-oxidant, and processing oil.

2. The curable composition of claim 1 wherein the copolymer has the general formula:



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wherein

R is hydrogen or a lower alkyl group;

R¹ is a monovalent organic group that is free of
 5 ethylenic-unsaturation and contains at least

one methylidyne group, $\begin{array}{c} | \\ -\text{CH} \\ | \end{array}$, having 4 to 30
 10 carbon atoms, optionally containing an oxygen
 or silicon atom that is catenated between
 carbon atoms,

a is an integer having a value of 3 to 7,
 inclusive;

15 x, y, and z are numbers designating the relative
 molar amounts of monomer units comprising the
 backbone chain of the copolymer the sum of
 (x + y + z) being about 35 to 400,000; z
 being 1 to 15% of the sum (x + y + z); y
 20 being 0 to 30% of the sum (x + y + z), and x
 being 70 to 99% of the sum (x + y + z).

3. The copolymer according to claim 2 wherein R¹
 has the structure



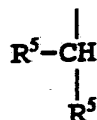
in which b is an integer having a value of 1
 to 5; Q is selected from a single bond, -O-,
 and divalent groups selected from the group
 35 consisting of an arylene group having 6 to 15
 carbon atoms, and



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in which each R⁴ is independently a lower alkyl group of 1 to 4 carbon atoms or R³; and R³ is a methylidyne group-containing group having the structural formula:

5



10

in which each R⁵ is independently an alkyl group having 1 to 4 carbon atoms or both R⁵s together provide an alkylene group forming with the methylidyne group to which it is attached a 5- or 6-membered ring of carbon atoms, with the proviso that when Q is arylene, R³ can also be methyl or ethyl and b can be zero.

15

4. The composition according to claims 1 to 3
20 wherein said copolymer has at least one of:
- a) a Tg in the range of -70 to 0°C,
 - b) an inherent viscosity in the range of 0.4 to 9.0 dl/g, and
 - c) a number average molecular weight in the
25 range of 5,000 to 50,000,000.

5. The E-beam or actinic radiation cured composition according to claims 1 to 4.

- 30 6. An article comprising a layer of the cured composition of claim 5 on at least one surface of at least one substrate.

7. The article according to claim 6 wherein said
35 substrate is selected from the group consisting of a polymeric layer, a fabric, a metal, paper, glass, ceramic, and a laminate of these materials.

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8. The article according to claims 6 or 7 which is a tape, a laminated structure, or an adhesive transfer film.

5 9. The tape according to claim 8 wherein said cured composition comprises the reaction product of ethylene, 1-hexene, and 4-methylpentene-1.

10 10. A method of preparing a radiation-cured saturated polyolefin pressure-sensitive adhesive comprising the steps of:

- a) providing a curable composition comprising a copolymer according to claims 1 to 5, and an effective amount of a photoactive crosslinking agent,
- 15 b) coating the composition onto a substrate,
- c) exposing the coated composition to actinic or E-beam radiation to effect crosslinking of the composition and provide said radiation-cured pressure-sensitive adhesive,
- 20 with the proviso that when the crosslinking is effected by actinic radiation there is present an effective amount of photoactive crosslinking agent.

INTERNATIONAL SEARCH REPORT

PCT/US 92/08710

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08J3/24; C09J7/02; C09J123/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C08J ; C09J ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,4 288 358 (J.R.TROTTER ET AL) 8 September 1981 cited in the application see column 1, line 47 - line 52 see column 2, line 64 - column 3, line 25 ---	1-4
A	EP,A,0 416 921 (MINNESOTA MINING AND MANUFACURING COMPANY) 13 March 1991 cited in the application see page 4, line 20 - line 58 see page 6, line 4 - page 7, line 12 ---	3-10
A	US,A,4 990 585 (T. KAWATA ET AL) 5 February 1991 cited in the application see column 1, line 33 - line 62 -----	1-4
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
12 JANUARY 1993	18. 01. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SCHMIDT H.R.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9208710
SA 65994

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4288358	08-09-81	None	
EP-A-0416921	13-03-91	US-A- 5112882 AU-B- 627347 AU-A- 6103890 CA-A- 2022616 JP-A- 3119084	12-05-92 20-08-92 14-03-91 07-03-91 21-05-91
US-A-4990585	05-02-91	JP-A- 63150307 US-A- 4942187	23-06-88 17-07-90

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